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Coordination Compounds of Lanthanides with 1,1-Dithiolate Ligands

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Abstract—Data on the syntheses and studies of the structures and properties of different types of coordination compounds of lanthanides with 1,1-dithiolate ligands (tris(chelates), complex salts, and heteroligand compounds) are considered. The results on the application of these compounds as precursors for the syntheses of lanthanide sulfides and the data on the photoluminescence, magnetic, and some other properties of a series of the complexes are presented.

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INTRODUCTION

Metal complexes with 1,1-dithiolate ligands bearing S-donor groups, namely, CS_2^- or PS_2^-, form one of important classes of coordination compounds interesting for the development of the chemistry of complex compounds and for practical use. The complexes with dithiocarbamate, xanthate, dithiophosphinate, and dithiophosphate ions as ligands containing various organic fragments are studied in most detail. These types of complexes were considered in a number of monographs [1, 2] and reviews [3–9]. Many of these complexes find diverse use (analytical chemistry, additives to lubricants and fuels, accelerators in vulcanization, fungicides, catalysts, precursors of metal sulfides, and others). Several acids bearing CS_2H or PS_2H fragments and salts containing 1,1-dithiolate anions are widely used in flotation and extraction.

The literature sources indicated contain a few information on the complexes of 1,1-dithiolate ligands, which are soft bases according to Pearson's principle of hard and soft acids and bases (HSAB), with lanthanide ions. Lanthanides (Ln) are classified as metals of group *a* (according to Chatt) or hard acids (according to the HSAB principle). Difficulties appeared when studying the interaction of the ligands (soft bases) with metals (hard acids), namely, an insufficient stability of the formed complexes, could be a reason for a small number of works on the syntheses of Ln complexes with 1,1-dithiolate ligands at the early stage of the investigation. Interest in the syntheses and studies of the Ln complexes with 1,1-dithiolate ligands has significantly increased within the recent 20 years due to the use of the complexes as precursors of lanthanide sulfides having important physical properties (magnetic, luminescent, and laser materials). In addition, attention was given to a series of valuable functional properties, in particular, photoluminescence (PL), of the complexes. It seems reasonable to consider published data on the syntheses, structures, and properties of the Ln complexes with ligands of this type *i*lated as solid phases. The present review contains only a brief volume of information on the properties of the complexes in solutions. The chemical formulas of the compounds mainly correspond to those presented in the text of the cited articles.

LANTHANIDE COMPLEXES CONTAINING DITHIOCARBAMATE LIGANDS

The most number of publications are devoted to the compounds containing dithiocarbamate ligands. This is related, most likely, to the fact that several salts of dithiocarbamic acids, especially $NaS_2CNEt_2 \cdot 3H_2O$, are accessible and fairly stable chemical reagents.

Tris(chelates) and complex salts. Tris(chelates) $Ln(Et_2NCS_2)_3$ and complex salts containing tetrakis(complexes) $Et_4N[Ln(Et_2NCS_2)_4]$ (Ln = La–Lu, except for Pm) were first synthesized and characterized [10, 11]. The tris(chelates) were synthesized by the reaction of anhydrous $LnBr_3$ with anhydrous NaS_2CNEt_2 in anhydrous EtOH, and then the solvent was removed in vacuo. Anhydrous acetonitrile was added to the residue, and a precipitate of NaBr was separated. Then diethyl ether was added to the solution, inducing the precipitation of the tris(chelate). The salts were obtained by the reaction of NaS_2CNEt_2, Et_4NBr, and $Ln(Et_2NCS_2)_3$ in anhydrous EtOH, and then the reaction mixtures were treated as in the synthesis of the tris(chelates). The compounds were synthesized and stored in a nitrogen atmosphere. It was found by X-ray phase analysis that the tris(chelates) formed two series of *i*structural complexes (Ln = La–Nd and Sm–Lu) and all complex salts were *i*structural. The unit cell parameters for $Et_4N[Eu(Et_2NCS_2)_4]$ are similar to those for $Et_4N[Np(Et_2NCS_2)_4]$ in which, according to the X-ray diffraction analysis data, the $Et_2NCS_2^-$ ions are bidentate chelating ligands and the coordination polyhedron S_8 of the Np atom is a distorted dodecahedron. Chelates $Ln(S_2CNEt_2)_3$ [12], $Ln(S_2CN(i\text{-}Pr)_2)_3 \cdot 2H_2O$, and $Ln(S_2CN(i\text{-}Bu)_2)_3$ (Ln = Nd, Er) [13, 14] were synthesized in an inert atmosphere using anhydrous $LnCl_3$ and NaS_2CNEt_2 in anhydrous EtOH. Since the metal chelates with 1,1-dithiolate ligands are used as precursors for the gas-phase chemical deposition of metal sulfide films, the sublimation behavior of the synthesized complexes were studied [12–14]. The chelates were found to be able to sublime in vacuo on heating with partial decomposition. The sublimed samples of $Ln(S_2CNEt_2)_3$ and $Ln(S_2CN(i\text{-}Bu)_2)_3$ are stable in air for at least 1–3 days. The reaction of $LnCl_3$ with sodium hexamethylenedithiocarbamate in anhydrous EtOH under a nitrogen atmosphere afforded chelates $Ln(C_6H_{12}NCS_2)_3$ (Ln = La, Pr, Nd, Sm, Tb, Dy) [15, 16]. The La(III) chelate is diamagnetic, and other compounds are paramagnetic: their effective magnetic moments are $\mu_{eff} = 3.62$ (Pr), 3.50 (Nd), 1.46 (Sm), 9.48 (Tb) and 10.40 (Dy) μ_B (300 K). The chelates exhibit photoluminescence (their spectra are omitted) [15] and volatile [16].

Complex salts $Et_3NH[Ln(i\text{-}Bu)_2NCS_2)_4]$ (Ln = La, Pr, Nd, Sm, Eu) were described in [17] almost simultaneously with [10, 11]. Solid $Ln(NO_3)_3 \cdot 6H_2O$ was added to a solution of $Et_3NH[(i\text{-}Bu)_2NCS_2)_4]$ in CH_2Cl_2. The obtained solution was separated by centrifugation from the solid phase (an excessive amount of lanthanide nitrate and a small amount of the aqueous phase), and the solid phase was washed with water and again centrifuged. A viscous product precipitated upon the addition of hexane to the solution. Its further washing with hexane resulted in the crystallization of the product, which was recrystallized from benzene. Unlike [10, 11], the synthesis was carried out in air. The solid phases of the compounds and their solutions in a series of organic solvents are stable. The magnetic susceptibilities of the obtained salts (solutions in $CDCl_3$, 293 K) were measured: $\mu_{eff} = 3.2$ (Pr), 3.3 (Nd), 1.5 (Sm), and 3.1 (Eu) μ_B. In addition, $Et_2NH_2[Ln(Et_2NCS_2)_4]$ and $Me_4N[Pr((i\text{-}Bu)_2NCS_2)_4]$ were synthesized [17]. The one-step reaction of $LnBr_3$, NaS_2CNEt_2, and Et_4NBr in MeCN under a nitrogen atmosphere was proposed for the synthesis of $Et_4N[Ln(Et_2NCS_2)_4]$ (Ln = La, Pr, Nd, Tb, Dy, Ho, Tm, Yb) [18]. Salts $Na[Ln(Et_2NCS_2)_4]$ (Ln = La–Yb, except for Pm) were obtained [19]. Anhydrous $LnCl_3$, NaS_2CNEt_2, and EtOH were used in the syntheses, and the necessity to use a nitrogen atmosphere was indicated only for the synthesis of the Ce(III) compound. The structure of $Na[La(Et_2NCS_2)_4]$ was determined by X-ray diffraction analysis. The $Et_2NCS_2^-$ ions are bidentate chelating ligands, the coordination polyhedron S_8 of the La atom is a distorted dodecahedron, and the average Ln–S distance is 2.97 Å. The thermal decomposition of $Na[Ln(Et_2NCS_2)_4]$ (Ln = La, Sm) gives La_2S_3 and a mixture of Sm_2S_3 and SmS, respectively [20]. The reaction of $LnCl_3$ and $NH_4S_2CNC_4H_8$ in THF afforded compounds $(C_4H_9O)[Ln(S_2CNC_4H_8)_4]$ (Ln = Ln, Nd) [21]. According to the X-ray diffraction data, the coordination of pyrrolidinedithiocarbamate ions results in the formation of the polyhedron LnS_8.

The synthesis under a dry nitrogen atmosphere and the properties of salts $Et_2NH_2[Ln(Et_2NCS_2)_4]$ (Ln = La–Lu, except for Pm) were described later [22]. According to the X-ray diffraction data, the coordination polyhedron LnS_8 in $Et_2NH_2[La(Et_2NCS_2)_4]$ is a distorted dodecahedron. Salts $Et_4N[Sm(S_2CNEt_2)_4]$ [23] and $Et_4N[La(S_2CNMe_2)_4]$ [24] were obtained. Salts $Me_2H_2N[Ln(Me_2NCS_2)_4]$ (Ln = La, Pr, Nd, Sm–Ho) were synthesized [25]. The X-ray diffraction data showed that in $Me_2H_2N[Nd(Me_2NCS_2)_4]$ the Nd atom had the coordination polyhedron S_8. Compound $Na[Eu(S_2CNMe_2)_4] \cdot 3.5H_2O$ was synthesized, which is photoluminescent but only at a low temperature (<100 K) [26]. The syntheses of salts $Et_2NH_2[La(S_2CNEt_2)_4]$ [27] and $Et_2NH_2[Pr(S_2CNEt_2)_4]$ [28] under a dry nitrogen atmosphere using anhydrous EtOH were supplemented by the determination of the thermodynamic and kinetic parameters of complex formation in an ethanolic solution. Unlike [10, 11], the authors [27, 28] did not use tris(chelates) in the syntheses of the salts but applied the reaction of Ln(III) chloride hydrates with $NH_4S_2CNEt_2$. The reaction of anhydrous $LnCl_3$ and piperidinium piperidinedithiocarbamate afforded salts $C_5H_{10}NH_2[Ln(C_5H_{10}NCS_2)_4]$ (Ln = La, Pr, Nd, Sm, Gd) [29].

Finally, the syntheses of salts $Et_2NH_2[Ln(S_2CNEt_2)_4]$ (Ln = Sm, Pr) in solutions of *i*propanol and ethanol, respectively, were described [30]. The authors did not mention the use of an inert atmosphere in the syntheses. Evidently, the stability of salts of the Ln tetrakis(complexes) depends considerably on the nature of organic groups in the ligand and on the type of the cation. It is most likely that the use of anhydrous reagents and solvents and inert atmosphere in the synthesis is not always necessary.

The salts containing tetrakis(complexes) were shown to be formed when monosubstituted dithiocarbamate anions were used as ligands [31, 32]. As a result, salts $RNH_3[Ln(RHNCS_2)_4]$ (R = Me, Et; Ln = La, Nd, Sm, Gd) [31] and $(Bu)_4N[Ln(RHNCS_2)_4] \cdot nH_2O$ (Ln = La–Gd, except for Pm; R = Ph, *p*-MePh; *n* = 0 or 2) were obtained [32].

The results of the preparation of nanoparticles of Ln sulfides by the thermolysis of the complex salts were published. Nanoparticles of Pr_2S_3 are formed upon the thermal decomposition of $Et_2NH_2[Pr(S_2CNEt_2)_4]$ [28]. The thermolysis of a solution of salt $Et_2NH_2[Eu(S_2CNEt_2)_4]$ in a mixture of oleylamine and Ph_3P gave nanoparticles of EuS for which the temperature of ferromagnetic ordering decreased with a decrease in the particle size [33]. The magnetic properties of the EuS nanocrystals obtained by the thermal decomposition of the salt containing the $[Eu(Et_2NCS_2)_4]^-$ ion in oleylamine and supported on polymer films were described [34]. Interestingly, nanocrystals of EuS ~10 nm in size with the luminescence properties are formed upon the photolysis of an acetonitrile solution of $Na[Eu(S_2CNEt_2)_4] \cdot 3.5H_2O$ at 25°C in air rather than upon thermolysis [35].

Heteroligand complexes. The instability in air of many compounds of the above described types impedes their study and application and stimulated the search for routes of the preparation of more stable complexes. The synthesis of heteroligand complexes based on 1,1-dithiolate ligands is a successful approach to the solution of this problem. The O- and N-donor organic ligands (hard bases) were used as additional ligands.

Compounds $Ln(S_2CNEt_2)_3(HMPA)_2$ (Ln = La, Pr–Gd, HMPA is hexamethylphosphotriamide) serve as examples for heteroligand complexes containing O-donor ligands [36]. The complexes were obtained by the reaction of $NaS_2CNEt_2 \cdot 3H_2O$, $LnCl_3 \cdot nH_2O$, and HMPA in anhydrous acetone in the presence of orthoethyl formate. According to the X-ray diffraction data, the coordination polyhedron of the La atom in $[La(S_2CNEt_2)_3(HMPA)_2]$ is O_2S_6 (distorted dodecahedron). Complex Er(*i*-$Pr_2NCS_2)_3(HMPA)$ was mentioned in [13], but the synthesis procedure was not presented. The $[La(THF)(H_2O)(S_2CNC_4H_8)_3]$ complex synthesized by the reaction of $LaCl_3$ with $La(S_2CNC_4H_8)_3 \cdot 2H_2O$ in THF was described [37]. According to the X-ray diffraction data, the La atom coordinates six atoms of three pyrrolidinedithiocarbamate ions and the O atoms of the water and THF molecules, and the LaO_2S_6 polyhedron is a distorted dodecahedron. Compounds $Ln(S_2CNMe_2)_3(DMSO)_2$ (Ln = La, Pr–Nd, Sm–Tb, DMSO is dimethyl sulfoxide) were synthesized [38]. According to the X-ray diffraction data, the LaO_2S_6 coordination polyhedron in $[La(S_2CNMe_2)_3(DMSO)_2]$ is a dodecahedron.

The most attention of researchers is given to the synthesis of heteroligand complexes containing nitrous heterocycles, especially 1,10-phenanthroline (Phen) and 2,2'-bipyridine (2,2'-Bipy), as additional ligands. The synthesis of complexes $Ln(S_2CNEt_2)_3(Phen)$ (Ln = Nd, Eu, Er) was reported [13], but the synthesis procedures were not presented. The complexes are volatile, but their thermal stability is insufficient. The reaction of $Ln(ClO_4)_3 \cdot nH_2O$, $R_2NCS_2NH_2Et_2$, and 2,2'-Bipy in MeCN afforded $Ln(Me_2NCS_2)_3(2,2'\text{-Bipy})$ (Ln = La, Pr, Nd, Sm–Yb, Y) [39] and $Ln(Et_2NCS_2)_3(2,2'\text{-Bipy})$ (Ln = La, Pr, Nd, Sm–Lu, Y) stable in air [40]. According to the X-ray diffraction data, the coordination polyhedron N_2S_6 of the Eu atom in the molecular structure of the mononuclear complex $[Eu(Me_2NCS_2)_3(2,2'\text{-Bipy})]$ is a distorted square antiprism, and $Me_2NCS_2^-$ and 2,2'-Bipy are bidentate chelating ligands [39]. In $[Er(Et_2NCS_2)_3(2,2'\text{-Bipy})]$ the coordination polyhedron N_2S_6 of the Er atom is a distorted dodecahedron, the Er–S bond lengths range from 2.746(1) to 2.845(1) Å, and the Er–N bonds are 2.515(1) and 2.547(1) Å [40]. Complexes $[Ln(Me_2NCS_2)_3(Phen)]$ (Ln = Pr, Nd, Gd) were *i*lated using Ln nitrates [41]. According to the X-ray diffraction data, all compounds contain the coordination polyhedron LnN_2S_6. The authors [39] synthesized compounds $Ln(Et_2NCS_2)_3(Phen)$ (Ln = La, Pr, Nd, Sm–Lu). The X-ray diffraction analysis indicates that the coordination polyhedron N_2S_6 of the Eu atom in $[Eu(Et_2NCS_2)_3(Phen)]$ is a distorted square antiprism. According to the data of electronic spectroscopy, the nephelauxetic ratios β for $Pr(Et_2NCS_2)_3(Phen)$ and $Sm(Et_2NCS_2)_3(Phen)$ are 0.9757 and 0.9958, respectively. The synthesis of complexes $Ln(Et_2NCS_2)_3(Phen)$ (Ln = La, Nd, Sm) using $LnCl_3 \cdot nH_2O$ and MeCN was described [42]. The reaction of NaS_2CNEt_2, Phen, and $LnCl_3$ in anhydrous EtOH afforded complexes $Ln(Et_2NCS_2)_3(Phen)$ [43]. Another synthesis of complexes $[Eu(S_2CNEt_2)_3(2,2'\text{-Bipy})]$ and $[Eu(S_2CNEt_2)_3(Phen)]$ was described in [44]. In this synthesis, acetone solutions of $Eu(NO_3)_3 \cdot 6H_2O$ and $Et_2NCS_2Na \cdot 3H_2O$ were mixed in air, precipitated $NaNO_3$ was filtered off, and orthoethyl formate and a solution of 2,2'-Bipy or Phen in acetone were added to the filtrate. The precipitate formed was filtered off and recrystallized. The complexes are stable in air. The X-ray diffraction data indicate the mononuclear structure of the complexes, and the coordination polyhedron N_2S_6 of the Eu atom is a deformed dodecahedron (Fig. 1). In the structure of $[Eu(S_2CNEt_2)_3(2,2'\text{-Bipy})]$, the Eu–S bond lengths range from 2.8042(1) to 2.8989(1) Å and the Eu–N bonds are 2.596(3) and 2.618(3) Å. Complexes $[Sm(2,2'\text{-Bipy})(S_2CNEt_2)_3]$ and $Sm(Phen)(S_2CNEt_2)_3$ stable in

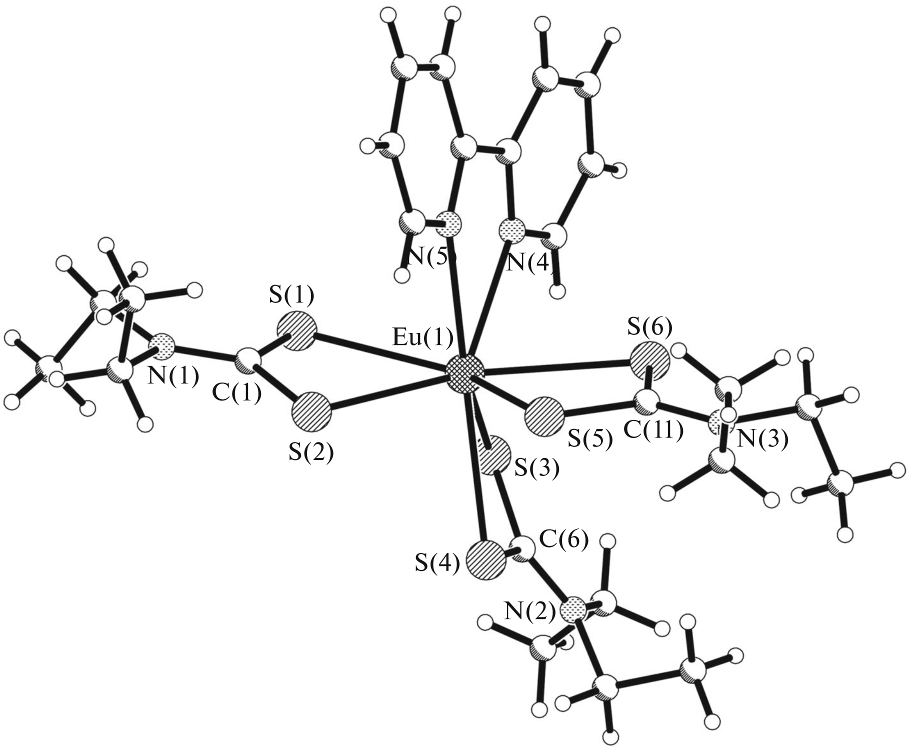

Fig. 1. Molecular structure of complex [Eu(S_2CNEt_2)$_3$(2,2'-Bipy)].

air were obtained [45]. The synthesis was carried out in MeCN in the presence of orthoethyl formate. According to the X-ray diffraction data, the molecular structure of [Sm(2,2'-Bipy)(S_2CNEt_2)$_3$] is similar to the structure [Eu(S_2CNEt_2)$_3$(2,2'-Bipy)]. The Sm–S bond lengths range from 2.808(2) to 2.909(1) Å, and the Sm–N bond lengths are nearly equal (2.616(7) and 2.616(6) Å). The Ln(*i*-Pr_2NCS_2)$_3$(Phen) (Ln = La, Pr, Nd, Sm–Lu) complexes were obtained [46]. According to the X-ray diffraction data, the coordination polyhedron NdN_2S_6 in [Nd(*i*-Pr_2NCS_2)$_3$(Phen)] is a distorted dodecahedron. Compounds Ln($S_2CNR'R''$)$_3$(Phen) (Ln = Sm, La; R' = Me, Et, R'' = *i*-Pr, Bu, *i*-Bu, heptyl, benzyl, and cyclohexyl) were *i*lated [47, 48]. An ethanolic solution of potassium dithiocarbamates and an aqueous solution containing $LnCl_3$ and Phen were used in the syntheses. The X-ray diffraction analysis showed that the coordination polyhedron LnN_2S_6 in the molecular structures [Ln($S_2CNEtBz$)$_3$(Phen)] was a distorted dodecahedron.

Success in the synthesis of heteroligand complexes stimulated the appearance of works on studying their thermodynamic properties. The thermochemistry (in particular, specific heat capacity, enthalpy of formation) of the compounds Tb(Et_2NCS_2)$_3$(Phen) [49], Pr(Et_2NCS_2)$_3$(Phen) [50], and Ln(Et_2NCS_2)$_3$(Phen) (Ln = La, Pr, Nd, Sm–Lu) [51, 52] was studied. The Tb(III) and Pr(III) complexes were synthesized by the reactions of $NaS_2CNEt_2 \cdot 3H_2O$, Phen · H_2O, and $LnCl_3 \cdot nH_2O$ in anhydrous EtOH [49, 50]. A similar synthesis method was used in [51, 52]. Later, the heat capacity was measured for Ln(Me_2NCS_2)$_3$(Phen) (Ln = La, Pr, Nd, Sm), and then the thermodynamic functions were calculated [53]. Attention was also given to the synthesis and study of the thermodynamic properties of the heteroligand complexes containing the heterocyclic pyrrolidinedithiocarbamate ion: Nd($C_4H_8NCS_2$)$_3$(Phen) [54], Ln($C_4H_8NCS_2$)$_3$ (Phen) (Ln = La, Pr, Nd, Sm) [55, 56], Eu($C_4H_8NCS_2$)$_3$(Phen) [57], and Ln($C_4H_8NCS_2$)$_3$(Phen) (Ln = La, Pr–Lu, except for Pm) [58]. The complexes studied in [54–58] were prepared in air by the reaction of $NH_4S_2CNC_4H_8$, $LnCl_3 \cdot nH_2O$, and Phen · H_2O in anhydrous EtOH.

The stability of the synthesized heteroligand complexes in air made it possible to start the studies of their possible use, in particular, as precursors of Ln sulfides. The compound [Eu(S_2CNEt_2)$_3$(Phen)] synthesized using a described procedure [44] was shown to be volatile and appropriate as a precursor for the preparation of thin films of EuS and $Zn_{1-x}Eu_xS$ by the gas-phase chemical deposition method (the temperature of the evaporator was 200–300°C, the temperature of the support was 460–530°C) [59–63]. It was found [64] that both $[Eu(S_2CNEt_2)_3(Phen)]$ and $[Ln(S_2CNEt_2)_3(Phen)]$ (Ln = Nd, Er, Yb) stable in air were volatile in a dynamic vacuum at 260–300°C. The compounds were synthesized in two steps using anhydrous $LnCl_3$, NaS_2CNEt_2, and Phen in dehydrated MeCN and MeOH. The thermal decomposition of the volatile complexes made it possible to obtain films of Ln sulfides. The crystal structure of the most volatile complex $[Yb(Phen)(S_2CNEt_2)_3]$ was studied. The coordination polyhedron N_2S_6 of the Yb atom is a distorted square antiprism, the Yb–S bond lengths range from 2.723(2) to 2.874(2) Å, and the Yb–N bond lengths are 2.497(6) and 2.539(6) Å [65]. The results obtained for the use of the heteroligand Ln complexes for the preparation of the corresponding sulfides stimulated the search for simpler synthesis methods. A promising available method for the preparation of complexes $[Ln(S_2CNEt_2)_3(Phen)]$, $[Ln(S_2CNMe(C_6H_{12}))_3(Phen)]$, and $[Ln(S_2CNC_5H_{10})_3(Phen)]$ (Ln = Eu, Er) by the reaction of $LnCl_3 \cdot 6H_2O$, Phen · H_2O, and sodium dithiocarbamate hydrate in an aqueous solution was proposed [66, 67]. The thermolysis of the complexes in dry nitrogen or at a low pressure gave crystals of EuS and Er_2S_3. This synthesis method was successfully used for the preparation of $[Ln(S_2CNEt_2)_3(Phen)]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Er, Yb, Lu) [68]. The vaporization process was studied for $[Pr(S_2CNEt_2)_3(Phen)]$ as an example using the Knudsen effusion method coupled with the mass spectral analysis of the gas phase. The saturated vapor was found to consist of Phen and $Pr(S_2CNEt_2)_3$ molecules. The results of studying the *i*thermal vacuum evaporation of the $[Ln(S_2CNEt_2)_3(Phen)]$ complexes allowed one to conclude that these compounds are promising for use as precursors for the preparation of functional materials by the gas-phase chemical deposition method [68].

The thermal decomposition at 180–300°C of the $[Sm(S_2CNEt_2)_3(2,2'\text{-Bipy})]$ and $[Sm(S_2CNEt_2)_3(Phen)]$ complexes accompanied by the pulverization of a solution of the complex in pyridine gave SmS films [69–72]. The synthesis procedures and characteristics of the compounds were described [72]. The reaction of anhydrous $SmCl_3$, NaS_2CNEt_2, and Phen (2,2'-Bipy) in anhydrous EtOH was used in the synthesis. It was found that the thermolysis of $[Nd(C_4H_8NCS_2)_3(Phen)]$ gave Nd_2S_3 [54], and EuS was the decomposition product of $[Eu(C_4H_8NCS_2)_3(Phen)]$ [57].

Both the known compounds $[Ln(S_2CNEt_2)_3(Phen)]$ (Ln = Nd, Sm, Gd, Ho, Er) and new complexes $[Eu(S_2CNRR')_3(Phen)]$ (R = Me, R' = Et, Pr, *i*-Bu) were synthesized using organic solvents (MeCN, MeOH) and water-organic mixtures [73]. The compounds are stable in air. According to the X-ray diffraction data, the coordination polyhedron EuN_2S_6 in the mononuclear Eu(III) complexes is a distorted square antiprism. In the crystals of the *i*structural compounds $[Ln(S_2CNEt_2)_3(Phen)]$, the Ln atoms also have the coordination polyhedron N_2S_6. The Ln–S and Ln–N bonds shorten in the Ln series on going from left to right, which correlates with a decrease in the ion radius of Ln. The study of the thermal properties of the Eu(III) complexes showed that the thermolysis in vacuo afforded EuS due to the redox reaction. Later, the thermolysis of complexes $[Ln(S_2CNEt_2)_3(Phen)]$ (Ln = La–Lu, except for Pm) placed in both a tube in vacuo and a sealed ampule was studied [74]. Regardless of the method, EuS is formed upon the decomposition of the Eu(III) complex. For complexes of other lanthanides, the composition of solid thermolysis products depends on the thermolysis conditions. The decomposition in vacuo of the Ln complexes of the beginning and middle of the series gives $\gamma\text{-}Ln_2S_3$ and Ln_2O_2S, whereas the decomposition of the Ln complexes of the end of the series produces a mixture of Ln_2O_2S and Ln_2O_3. The decomposition of the Ce(III) complex gave CeO_2. In the case of the Tb(III), Tm(III), Yb(III), and Lu(III) complexes, the decomposition in an ampule produces Ln_2O_2S. The complexes of other Ln decompose to form Ln_2S_3.

Considerable attention is given to the preparation of nanosized particles of Ln sulfides when using the heteroligand Ln complexes with dithiocarbamate ligands as precursors because of the development of nanomaterial synthesis. The preparation of EuS nanoparticles is of special interest. For example, the preparation of EuS particles using $[Eu(Phen)(S_2CNEt_2)_3]$ synthesized in an aqueous solution according to a known procedure [67] was described [75]. For the thermal decomposition of the solid complex in a nitrogen flow at 430°C, the particle size was 50–120 nm. A mixture of the complex with oleylamine was heated in a nitrogen atmosphere at 200°C to form EuS nanocrystals 5–6 nm in size. The presence of oleylamine prevents nanoparticle agglomeration. Continuing the studies, the authors of [76] carried out the decomposition of mixtures of the $[Eu(Phen)(S_2CNEt_2)_3]$ or $[Eu(2,2'\text{-Bipy})(S_2CNEt_2)_3]$ complexes with oleylamine at 260–330°C and obtained EuS nanocrystals, whose sizes depended on the precursor and decomposition conditions and ranged from 2.6 to 20 nm. The size was found to affect the optical and magnetic properties of the nanocrystals. The preparation of the EuS nanocrystals due to the thermal decomposition in argon at 280°C of the same complexes in the presence of trioctylphosphine and oleylamine, as well as octadecene, was described [77, 78]. The decomposition of $[Eu(S_2CNEt_2)_3(2,2'\text{-Bipy})]$ produces nanoparticles with sizes of 9–23 nm [78]. The decomposition of a solution of $[Eu(S_2CNEt_2)_3(Phen)]$ (synthesized in an aqueous solution according to [66]) in oleylamine at 315°C in a nitrogen atmosphere gave nanocrystals with a size of ~8 nm [79]. In addition, the nanocomposite based on polystyrene and EuS was obtained [79], and its magnetic properties differ from the properties of the EuS nanocrystals. A solution of $[Eu(S_2CN(i\text{-}Bu)_2)_3(Phen)]$ was heated in a mixture of trioctylphosphine and oleylamine at 240°C to form EuS nanoparticles ~20 nm in size for which magnetic ordering was observed [80].

Polycrystalline powders $Eu_{1-x}Gd_xS$ (x = 0.003–1.0) were obtained by the thermal decomposition of a mixture of $[Eu(S_2CNEt_2)_3(Phen)]$ and $[Gd(S_2CNEt_2)_3(Phen)]$ in a sealed tube at 700°C [81]. In addition, nanoparticles of $Eu_{0.982}Gd_{0.018}S$, whose average size was 16.7 nm, were obtained by the decomposition of a solution of these precursors in a mixture of oleylamine and Ph_3P at 265°C. The magnetic measurements showed that a decrease in the particle size resulted in a decrease in the Curie temperature. The authors [82] used published procedures [67, 75] to obtainin aqueous solutions $[Gd(S_2CNEt_2)_3(2,2'\text{-}Bipy)]$ and compounds in which the dithiocarbamate ligands contained fragments of the nitrous heterocycles: $[Eu(S_2CNC_4H_8)_3(2,2'\text{-}Bipy)]$, $[Eu(S_2CNC_5H_{10})_3(2,2'\text{-}Bipy)]$, $[Eu(S_2CNC_5H_9Me)_3(Phen)]$, and $[Gd(S_2CNC_4H_8)_3(2,2'\text{-}Bipy)]$. According to the X-ray diffraction data, the structures of all the five mononuclear compounds contain the LnN_2S_6 polyhedron. The thermal decomposition of a suspension of the $[Ln(S_2CNC_4H_8)_3(2,2'\text{-}Bipy)]$ (Ln = Eu, Gd) complexes in an oleylamine–trioctylphosphine mixture at 290°C in a nitrogen atmosphere gave nanocrystals of $Eu_{1-x}Gd_xS$ with a maximum Curie temperature of 29.4 K.

An important achievement in the study of the functional properties of the Ln complexes was the observation of PL at both a low temperature (salt $Na[Eu(S_2CNMe_2)_4] \cdot 3.5H_2O$ [26]) and room temperature. The authors [83] pioneered in finding that the heteroligand Eu(III) dithiocarbamate complexes showed PL at 300 K. The red fluorescence of the $[Eu(Et_2NCS_2)_3L]$ (L = Phen, 2,2'-Bipy) and $[Eu(Ph_2NCS_2)_3Phen]$ complexes at 77 and 300 K and the phosphorescence of similar Gd(III) complexes at 77 K in the solid phase were studied. These complexes were synthesized by the reaction of the hydrated Eu(III) or Gd(III) salt with the dithiocarbamate salt and nitrous heterocycle in a mixture of organic solvents. The energies of the lowest triplet levels of the $Ph_2NCS_2^-$ and $Et_2NCS_2^-$ ligands equal to 20877 and 19120–20012 cm^{-1} (depending on the composition of the complex), respectively, were determined from the excitation and emission spectra of the Gd(III) and Eu(III) complexes [83]. The relative quantum yields for $[Eu(Et_2NCS_2)_3Phen]$ and $[Eu(Ph_2NCS_2)_3Phen]$ at 300 K are 10.4 and 10.5%, respectively. For the Eu(III) complexes, the values of β range from 0.9953 to 0.9991. It is most likely that the covalent contribution to the Eu–ligand bonds is insignificant.

The heteroligand complexes $[Ln(S_2CNR_2)_3L]$ (Ln = Pr, Sm; R = *i*-Bu, Bz, Et; L = Phen, 2,2'-Bipy, 5-chloro-1,10-phenanthroline (Cphen)) were synthesized by the reaction of salt Ln(III) hydrate with ammonium or sodium dithiocarbamate and nitrous heterocycle in an organic or a water-organic solution [30]. In addition, the complex salts $Et_2NH_2[Ln(S_2CNEt_2)_4]$ (Ln = Pr, Sm) were obtained by the reaction of $Et_2NH_2S_2CNEt_2$ and $Ln(NO_3)_3 \cdot 6H_2O$ in EtOH (Pr) or *i*-PrOH (Sm). According to the X-ray diffraction data, the crystal structures of complexes $[Sm(S_2CN(i\text{-}Bu)_2)_3L]$, $[Pr(S_2CNEt_2)_3(Phen)]$, and $[Pr(S_2CN(i\text{-}Bu)_2)_3L]$ consist of molecules of the mononuclear complex, and the LnN_2S_6 coordination polyhedron is a distorted dodecahedron. The values of β equal to 0.9877–0.9911 and 0.9705–0.9745 were calculated by an analysis of the electronic spectra of the Sm(III) and Pr(III) complexes, respectively. These values are close to the published results [39]. It was concluded that the ionic contribution to the Ln(III)–ligand bonds predominated. The ionicity of the bonds increases on going from light to heavy lanthanides, while the covalence of the bonds somewhat increases on going from the heteroligand complexes to salts of the tetrakis(chelates). The PL of the above described complexes, $[Ln(S_2CNEt_2)_3Phen]$ (Ln = Eu, Tb, Dy), and complex salts $Et_2NH_2[Ln(S_2CNEt_2)_4]$ (Ln = La, Gd) in MeCN at 300 K was described. The energy of the lowest triplet level of the $Et_2NCS_2^-$ ion, equal to 23095 cm^{-1}, was determined from the phosphorescence spectra of salts $Et_2NH_2[Ln(S_2CNEt_2)_4]$ (Ln = La, Gd). It was found in the series of compounds $[Ln(S_2CNEt_2)_3(Phen)]$ that the Sm(III) complex in MeCN had the highest PL intensity (I) (the most intense bands are observed at λ_{max} = 601 and 646 nm) compared to the Eu(III) and Tb(III) complexes. This is unusual, since it is known that the most intense PL is observed for the Eu(III) and Tb(III) complexes in the case of the Ln compounds with the O- and N-containing ligands. The authors assumed that the reduction properties of the $Et_2NCS_2^-$ ligand, resulting in the possible reduction of the Eu^{3+} ions to Eu^{2+}, can be a reason for the lower PL intensity of the Eu(III) complex. For the complexes $[Ln(S_2CNEt_2)_3L]$ in the case of Sm(III), the PL intensity changes depending on L as follows: Cphen < 2,2'-Bipy < Phen; in the case of Pr(III): Cphen < 2,2'-Bipy ≈ Phen. It was found that the nature of the substituent in the dithiocarbamate ion also significantly contributed to the PL of the complex. For example, the PL intensity I of the complexes $[Ln(S_2CNR_2)_3(Phen)]$ (Ln = Sm, Pr) increases in the series *i*-Bu < Et < Bz. A comparin of the PL spectra of the heteroligand complexes $[Ln(S_2CNEt_2)_3(Phen)]$ (Ln = Sm, Pr) and complex salts $Et_2NH_2[Ln(S_2CNEt_2)_4]$ (Ln = Sm, Pr) shows that the PL intensity of the complexes containing Phen is higher than I of the salts containing the

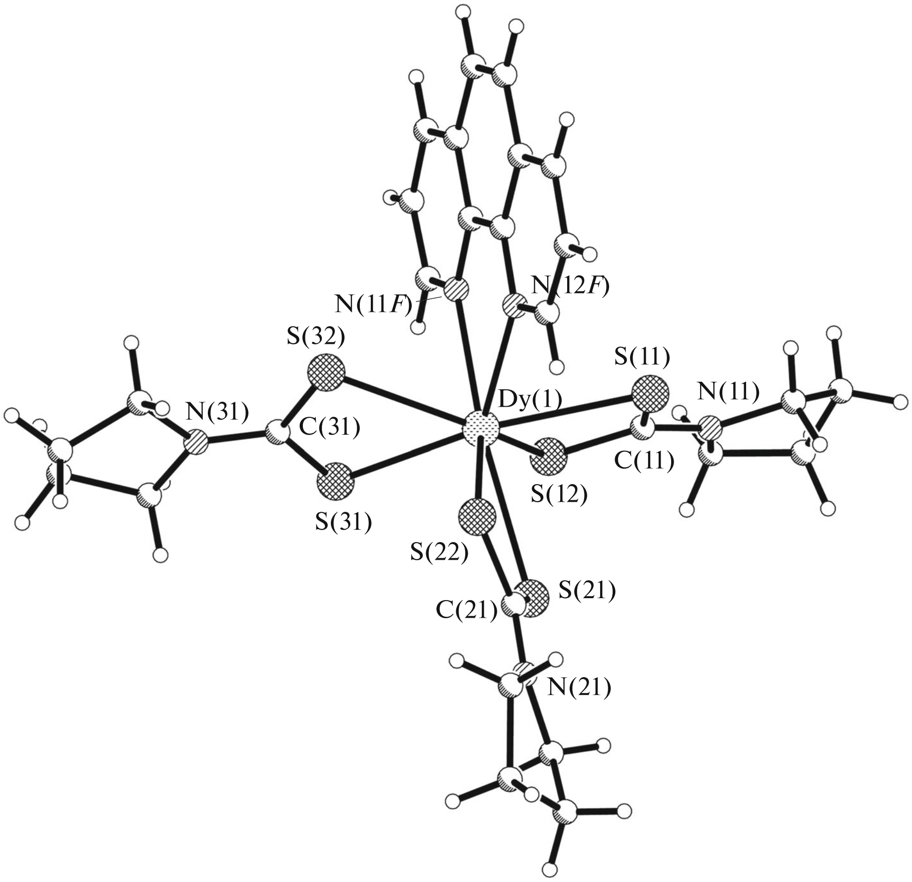

Fig. 2. Molecular structure of complex [Dy(Phen)($C_4H_8NCS_2$)$_3$] · $3CH_2Cl_2$.

tetrakis(chelates). Since the studied complex salts show the PL, the $Et_2NCS_2^-$ ligand is capable of energy transferring from the lowest triplet level of the ligand to the emission level of the Ln^{3+} ion. The relative PL quantum yields of the complexes [Ln(S_2CNEt_2)$_3$(Phen)] (Ln = Sm, Pr) are 11 ± 2 and 0.9 ± 0.5%, respectively [30].

The magnetic and photoluminescence properties of the complexes [Ln(Phen)($C_4H_8NCS_2$)$_3$] and solvate compounds [Ln(2,2'-Bipy)($C_4H_8NCS_2$)$_3$] · $0.5CH_2Cl_2$ (Ln = Sm, Eu, Tb, Dy, Tm) were studied [84, 85]. The [Ln(Phen)($C_4H_8NCS_2$)$_3$] complexes were synthesized using a procedure different from that described in [58] by a choice of the initial salts and solvents (*i*-PrOH was used instead of anhydrous EtOH). The compounds [Ln(2,2'-Bipy)($C_4H_8NCS_2$)$_3$] · $0.5CH_2Cl_2$ were synthesized by the reaction of hydrated Ln nitrates, $C_4H_8NCS_2NH_4$, and 2,2'-Bipy in a CH_2Cl_2–*i*-PrOH mixture. According to the X-ray diffraction data, for the mononuclear complexes, in the crystal structures of the solvates [Dy(Phen)($C_4H_8NCS_2$)$_3$] · $3CH_2Cl_2$ [84] (Fig. 2) and [Sm(2,2'-Bipy)($C_4H_8NCS_2$)$_3$] · $0.5CH_2Cl_2$, each Ln atom coordinates six S atoms of three bidentate chelating $C_4H_8NCS_2^-$ ligands and two N atoms of the bidentate chelating N-heterocycle to form the coordination polyhedron LnN_2S_6, which is a distorted dodecahedron and a tetragonal antiprism, respectively. It was found by the X-ray phase analysis that the compounds were *i*structural in the series of complexes [Ln(Phen)($C_4H_8NCS_2$)$_3$] and [Ln(2,2'-Bipy)($C_4H_8NCS_2$)$_3$] · $0.5CH_2Cl_2$. As established by the static magnetic susceptibility method, the studied temperature dependences of μ_{eff} of the solid phases of the compounds in a range of 2–300 K are characteristic of the complexes of Ln^{3+} ions (Fig. 3). It was established that [Tb(Phen)($C_4H_8NCS_2$)$_3$] and [Dy(2,2'-Bipy)($C_4H_8NCS_2$)$_3$] · $0.5CH_2Cl_2$ at 2 K were transited to the magnetically ordered state (Fig. 4). The study of the PL of the complexes in the solid phase at 300 K shows that for [Ln(Phen)($C_4H_8NCS_2$)$_3$] the PL intensity decreases in the series $Sm^{3+} > Tb^{3+} \gg Eu^{3+} \approx Dy^{3+}$, and the complex of the Tm^{3+} ion do not exhibit PL (Fig. 5) [84]. The Sm(III) complex show the red-orange PL (the spectrum has the most intense bands at λ_{max} = 601 and 646 nm). A similar character of chang-

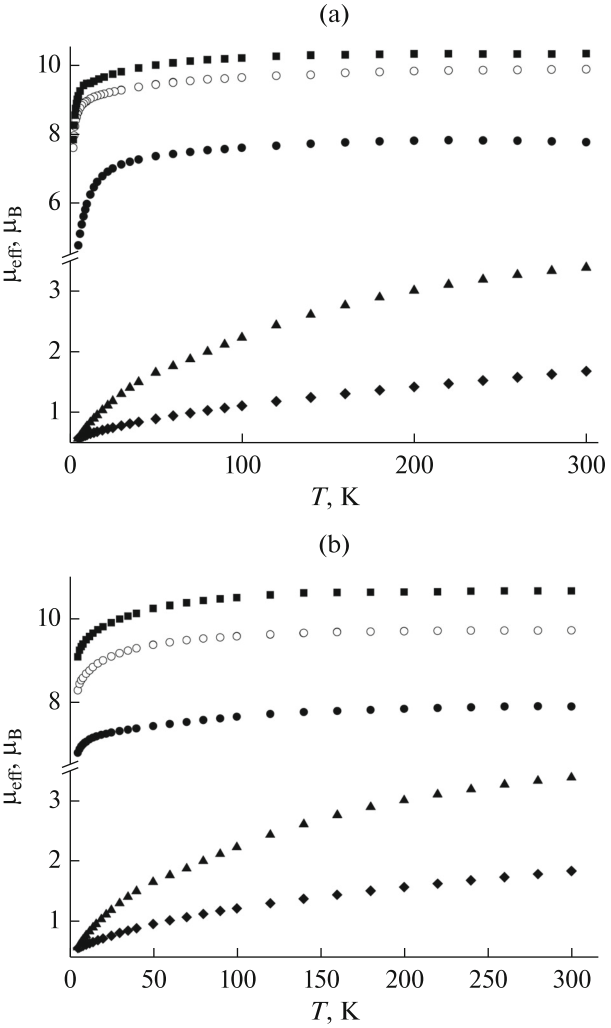

Fig. 3. Plots $\mu_{\text{eff}}(T)$ for complexes (a) $[Ln(Phen)(C_4H_8NCS_2)_3]$, where Ln = (◆) Sm, (▲) Eu, (○) Tb, (■) Dy, and (●) Tm and (b) $[Ln(2,2'\text{-}Bipy)(C_4H_8NCS_2)_3] \cdot 0.5CH_2Cl_2$, where Ln = (◆) Sm, (▲) Eu, (○) Tb, (■) Dy, and (●) Tm.

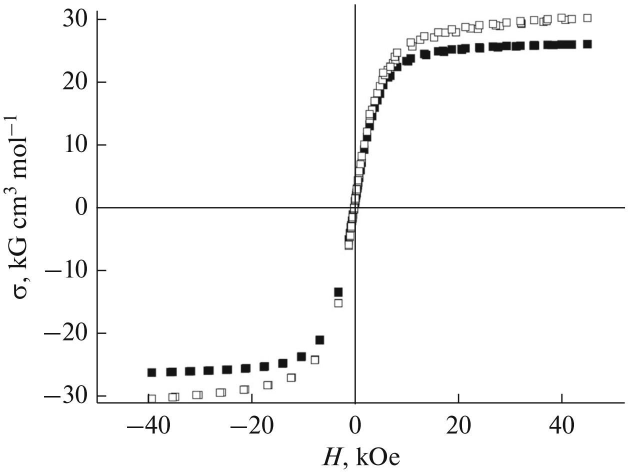

Fig. 4. Magnetization (σ) of complexes (■) $[Tb(Phen)(C_4H_8NCS_2)_3]$ and (□) $[Dy(2,2'\text{-}Bipy)(C_4H_8NCS_2)_3] \cdot 0.5CH_2Cl_2$ vs. external magnetic field strength (*H*).

ing *I* of PL is also observed for the compounds $[Ln(2,2'\text{-}Bipy)(C_4H_8NCS_2)_3] \cdot 0.5CH_2Cl_2$: the compound of the Sm^{3+} ion has the highest PL intensity, whereas the complexes of the Eu^{3+}, Dy^{3+}, and Tm^{3+} ions do not luminesce at all [85]. In addition, it was found that the Phen-containing Sm(III) compound exhibited the more intense PL than the Sm(III) complex containing 2,2'-Bipy [86]. The demonstration of the most intense PL by the Sm(III) complexes coincides with the published data [30].

Complexes $[Ln(C_5H_{10}NCS_2)_3(Phen)]$ (Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er) were obtained by the addition of a solution of sodium piperidinedithiocarbamate and Phen in MeOH to a solution of Ln(III) chloride hydrate in EtOH [87]. The single crystals of compounds $[Ln(C_5H_{10}NCS_2)_3(Phen)] \cdot CHCl_3$ (Ln = Pr, Nd, Sm) were grown. According to the X-ray diffraction data, these compounds are *i*structural, and the coordination polyhedron LnN_2S_6 in the mononuclear complexes is a distorted dodecahedron. At room temperature, solutions of the complexes of Dy^{3+}, Sm^{3+}, Tb^{3+}, and Pr^{3+} ions in MeCN show the PL, and the most intense emission is observed for the compounds of the first two ions. It was shown [87] that *I* of PL of the complex $[Sm(C_5H_{10}NCS_2)_3(Phen)]$ was higher than *I* of $[Sm(C_5H_{10}NCS_2)_3(2,2'\text{-}Bipy)]$. In addition, the compar*i*n of *I* of PL for the complexes $[Sm(A)_3(Phen)]$ (A is piperidinedithiocarbamate, azepanedithiocarbamate, and pyrrolidinedithiocarbamate ions) showed that the complex containing pyrrolidinedithiocarbamate ions had the highest PL intensity.

Other interesting functional properties of the heteroligand Ln complexes containing dithiocarbamate ligands were also observed. The addition of a small amount of the complexes $[Ln(Et_2NCS_2)_3(Phen)]$ (Ln = La, Nd, Sm) was found to improve the properties of the antiwear lubricant [42]. Compounds $Ln(R_2NCS_2)_3(Phen)$ (Ln = Eu, Yb, Gd, Er, Nd; R = Et, Ph) obtained using a described procedure [83] efficiently catalyze the cyanosilylation of aldehydes [88]. Complex $[Eu(Et_2NCS_2)_3(Phen)]$ was used as a component of the catalytic system in the asymmetric synthesis of cyanohydrins [89]. Complexes $[Ln(C_5H_{10}NCS_2)_3(Phen)]$ (Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er) and $[Ln(C_6H_{12}NCS_2)_3(Phen)]$ (Ln = La—Nd, Sm, Gd—Dy, Er) containing azepanedithiocarbamate ligands are catalysts in the trimethylsilylcyanation of carbonyl compounds [87, 90].

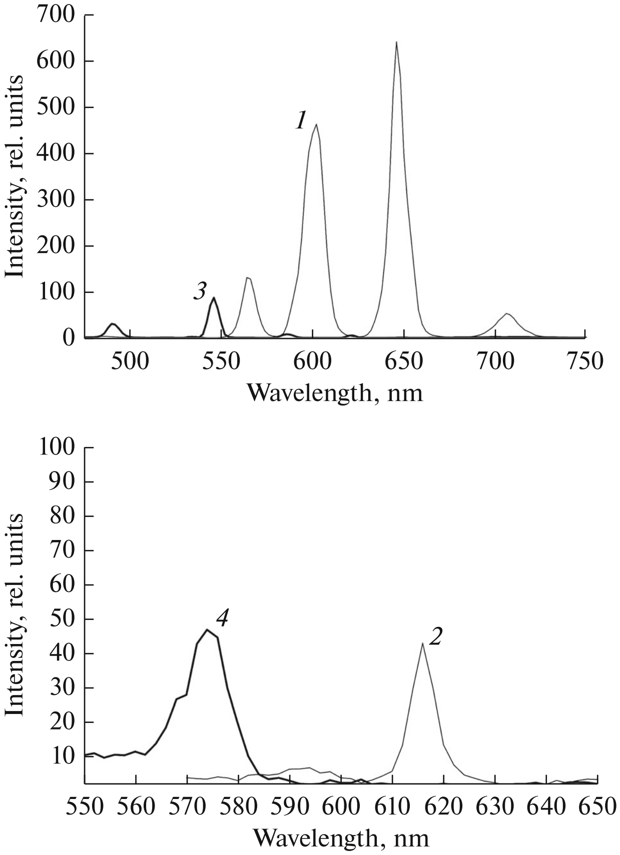

Fig. 5. PL spectra of complexes $[Ln(Phen)(C_4H_8NCS_2)_3]$ (Ln = (*1*) Sm, (*2*) Eu, (*3*) Tb, and (*4*) Dy).

LANTHANIDE COMPLEXES CONTAINING XANTHATE LIGANDS

There are a small number of Ln compounds with xanthate ligands. The interaction of Ln^{3+} and $ROCS_2^-$ ions (Ln = Eu, Nd; R = Et, *i*-Pr, *i*-Bu, *i*-Am) in MeCN was studied [91]. The formation of tetrakis(chelates) $[Ln(S_2COEt)_4]^-$ was established using the electronic spectra. The coordination number of Ln equal to 8 was assumed for these complexes due to the bidentate chelating coordination mode of the xanthate ligands. Complex salts $Et_4N[Ln(S_2COEt)_4]$ (Ln = La, Sm) were *i*lated by mixing a solution of anhydrous $Ln(NO_3)_3$ and $EtOCS_2K$ in anhydrous acetone and a solution of Et_4NCl in anhydrous MeCN. The thermal destruction of these hygroscopic salts in an inert atmosphere was studied [91, 92]. The La(III) compound is less stable than the Sm(III) complex, and its decomposition gives La_2S_3. A mixture of SmS and Sm_2S_3 was found as a result of the thermolysis of the Sm(III) salt. The thermolysis of these salts was assumed [91, 92] to be accompanied by the formation of volatile tris(chelates) $Ln(S_2COEt)_3$. The synthesis of tris(chelates) $La(ROCS_2)_3$ (R = *o*-, *m*-, and *p*-MeC_6H_4; $PhCH_2$) has recently been described [93]. The chelates were synthesized by the reaction of $ROCS_2Na$ with $LaCl_3 \cdot 7H_2O$ in MeOH under anhydrous conditions. In addition, heteroligand complexes $La(ROCS_2)_3L_2$ (L = Py or Ph_3P), $La(ROCS_2)_3L$ (L = 2,2'-Bipy or Phen) were synthesized by the reaction of the tris(chelates) and additional L ligands in MeOH [93]. It was concluded on the basis of the data of NMR, mass, and IR spectroscopies that the La atom in the tris(chelates) had a coordination number of 6, whereas the coordination number in the heteroligand complexes is 8. The thermolysis of La(*p*-$MeC_6H_4OCS_2)_3$ affords LaS_2. Complex $La(PhCH_2OCS_2)_3(Phen)$ exhibits a high antimicrobial activity.

The authors [94] proposed an explanation of a low stability of the Ln xanthate complexes during the synthesis in the presence of moisture. In their opinion, this is related to the fact that the O atom (sterically more accessible than the N atom in $R_2NCS_2^-$) in the coordinated xanthate ligand can be a potential object for the electrophilic attack by water molecules, resulting in the solvolysis of the ligand accompanied by its destruction.

LANTHANIDE COMPLEXES CONTAINING DITHIOPHOSPHINATE LIGANDS

Tris(chelates) and complex salts. The possibility of preparing the salt $Ph_4P[Pr(S_2PMe_2)_4]$ containing the tetrakis(complex) was indicated in [95]. The synthesis of this compound by the reaction of $PrCl_3 \cdot 6H_2O$, NaS_2PMe_2, and Ph_4PBr in EtOH was described later and its crystal structure was studied [96]. The Pr atom was found to coordinate four bidentate chelating $Me_2PS_2^-$ ligands, forming the polyhedron PrS_8 as a distorted tetragonal antiprism. A similar procedure of the synthesis but under a nitrogen atmosphere was used for the preparation of salts $Ph_4P[Ln(S_2PMe_2)_4]$ (Ln = La–Lu, except for Pm) [97]. Salts $Ph_4As[Ln(S_2P(C_6H_{11})_2)_4]$ (Ln = La–Nd) were *i*lated from an ethanolic solution of $LnCl_3 \cdot nH_2O$, $NH_4S_2P(C_6H_{11})_2$, and Ph_4AsCl without a nitrogen atmosphere [97]. An attempt to obtain Ln(III) tris(chelates) with $Me_2PS_2^-$ ions failed, but tris(chelates) $[Ln(S_2P(C_6H_{11})_2)_3]$ (Ln = Pr, Nd, Sm–Lu) with the $(C_6H_{11})_2PS_2^-$ ligand were *i*lated from an ethanolic solution in air. The hygroscopicity of the complexes increases on moving along the Period from light to heavy Ln [97]. The complexes with $(C_6H_{11})_2PS_2^-$ ions are less sensitive to air moisture than the complexes with $Me_2PS_2^-$ ions.The compar*i*n of the synthesis procedures for these tris(chelates) with the procedures for similar dithiocarbamate complexes indicates that the dithiophosphinate complexes are less hygroscopic [97]. An analysis of the electronic spectra made it possible to obtain the values of β for tris(chelates) $[Ln(S_2P(C_6H_{11})_2)_3]$ (Ln = Pr, Nd, Sm, Dy, Ho, Er, Tm) equal to 0.968–0.991. For the synthesized complex salts, the values of β range from 0.975 to 0.996. The values obtained for β are close to those presented for the complexes with the dithiocarbamate ligands [30, 39, 83]. It is most likely that the ionic contribution to the Ln–ligand bonds also predominates in the complexes with the dithiophosphinate ligands. The data of IR spectroscopy and X-ray phase analysis allowed the authors [97] to conclude that the tris(chelates) with light and heavy Ln form two structural types. The X-ray diffraction analysis shows that the complexes $[Ln(S_2P(C_6H_{11})_2)_3]$ (Ln = Pr, Sm) are mononuclear and the coordination polyhedron LnS_6 is a distorted trigonal prism [98]. The Pr–S and Sm–S average bond lengths are 2.84 and 2.79 Å, respectively. The difference in two structural types is that the Pr(III) complex includes an additional rotation of one ligand around the 2-fold axis. The crystal structure of the tris(chelates) $[Ln((C_6H_{11})_2PS_2)_3]$ (Ln = Dy, Lu) was determined later [99]. The Ln atoms in these compounds coordinate six S atoms to form a coordination polyhedron intermediate between trigonal prism and octahedron. Unlike [97], the authors [100] succeeded to obtain very hygroscopic tris(chelates) $Ln(Me_2PS_2)_3$ (Ln = Pr, Nd, Eu), which are monomeric in $CHCl_3$, by the reaction of $LnCl_3$ with $Me_2PS_2Na \cdot 2H_2O$ in anhydrous EtOH. The octahedral structure of these complexes was assumed. The values of μ_{eff} of the complexes at ~295 K are 3.72 (Pr), 3.74 (Nd), and 3.15 (Eu) μ_B. The reaction of Et_2PS_2Na and $Pr(NO_3)_3$ in anhydrous EtOH on heating to 70°C afforded hygroscopic $Pr(Et_2PS_2)_3$ [101].

The syntheses and structures of the Ln(III) complexes (Ce, Nd, Sm, Eu, Gd, Dy, and Yb) with $Ph_2PS_2^-$ ions were described [102]. The reactions of dehydrated $LnCl_3$ with $NH_4S_2PPh_2$ and Ph_4PCl or Et_4NCl in MeCN under an inert atmosphere gave compounds of different compositions, depending on the nature of Ln(III). Complex salts $Et_4N[Ln(S_2PPh_2)_4]$ (Ln = Ce, Nd) and $Ph_4P[Ln(S_2PPh_2)_4]$ (Ln = Sm, Eu) were obtained with Ln^{3+} ions having a larger radius (Ln = Ce, Nd, Sm, Eu). Under these conditions, Yb^{3+} ion forms complex $Ph_4P[Yb(S_2PPh_2)_3Cl]$. According to the X-ray diffraction data, in $[Ln(S_2PPh_2)_4]^-$anions (Ln = Ce, Nd, Sm, Eu) and in earlier obtained salts $Ph_4P[Ln(S_2PMe_2)_4]$ (Ln = Sm, Eu), the Ln^{3+} ion coordinates eight S atoms of the bidentate chelating $Ph_2PS_2^-$ ligands. In the tetrakis(chelate) of the salt $Ph_4P[Sm(S_2PPh_2)_4]$, the Sm–S bond lengths (2.90(2) and 2.93(2) Å) significantly exceed the bond lengths in the tris(chelate) $[Sm(S_2P(C_6H_{11})_3]$ [98]. The Yb^{3+} ion of a shorter radius coordinates six S atoms and one Cl atom.

Heteroligand complexes. The preparation of the heteroligand complexes due to the introduction of additional ligands, especially bidentate N-heterocycles, turned out to be a successful method of stabilization for both dithiophosphinates and dithiocarbamates of Ln(III).

A series of adducts based on tris(chelates) $Ln(Me_2PS_2)_3$ was synthesized [103]. The adduct $Pr(Me_2PS_2)_3 \cdot 2Py$ was obtained by the addition of pyridine to a solution of thoroughly dehydrated $Pr(Me_2PS_2)_3$ in anhydrous benzene followed by the short-term heating of the mixture to 60°C, and then pyridine was additionally poured to the mixture. The adduct $Pr(Me_2PS_2)_3 \cdot 2MeOH$ was obtained using a solution of $Pr(Me_2PS_2)_3$ in MeOH. The values of μ_{eff} for these adducts at ~303 K are 3.62 and 3.58 μ_B, respectively. The reaction of $La(NO_3)_3 \cdot 6H_2O$ with Me_2PS_2Na in anhydrous ethanol affords compound $La(Me_2PS_2)_3 \cdot 2H_2O$. The synthesis of the adduct $Pr(Me_2PS_2)_3 \cdot 2Et_2NH$ by the addition of an Et_2NH excess to a solution of $Pr(Me_2PS_2)_3$ in $CHCl_3$ was described [101]. The adduct $Nd((CH_3OC_6H_4)MePS_2)_3 \cdot 2Py$ was synthesized similarly [101]. Compounds $Ln(S_2PPh_2)_3(MeCN)_2$ were *i*lated for Ln^{3+} ions of a medium radius (Ln = Gd, Dy) [102]. According to the X-ray diffraction data, in these compounds the Gd^{3+} and Dy^{3+} ions coordinate six S atoms and two N atoms of the MeCN molecules.

The stable heteroligand compounds $[Ln(L)(i\text{-}Bu_2PS_2)_3]$ (Ln = Pr, Nd, Sm, Eu; L = Phen, 2,2'-Bipy) are formed in air by the reaction in organic solvents of Phen or 2,2'-Bipy with the Ln(III) tris(chelates) preliminarily obtained in the solution by the exchange decomposition between Ln(III) nitrates and $i\text{-}Bu_2PS_2Na$ [104]. The solvent for the preparation of complexes $[Ln(Phen)(i\text{-}Bu_2PS_2)_3]$ (Ln = Pr, Nd) was *i*-PrOH, whereas MeCN served as a solvent in the synthesis of the Sm(III) and Eu(III) complexes. According to the X-ray diffraction data, the crystal structures of complexes $[Eu(L)(i\text{-}Bu_2PS_2)_3]$ consist of molecules of the mononuclear complexes in which the coordination polyhedron N_2S_6 of the Eu atom is a distorted dodecahedron (Fig. 6). The $i\text{-}Bu_2PS_2^-$, Phen, and 2,2'-Bipy ligands are bidentate chelating. The crystal structures of these compounds were shown to contain dimeric ensembles of molecules of the $[Eu(L)(i\text{-}Bu_2PS_2)_3]$ complexes formed by van der Waals interactions and a weak hydrogen bond.

The complex $[Y(Phen)(i\text{-}Bu_2PS_2)_2(NO_3)]$ containing not two but three types of ligands was synthesized later [105]. In the synthesis, the solvent was MeCN and orthoethyl formate was added to prevent hydrolysis. An attempt to obtain a complex containing no nitrato groups due to an increase in the concentration of the sulfur-containing ligand was unsuccessful. According to the X-ray diffraction data, the crystal

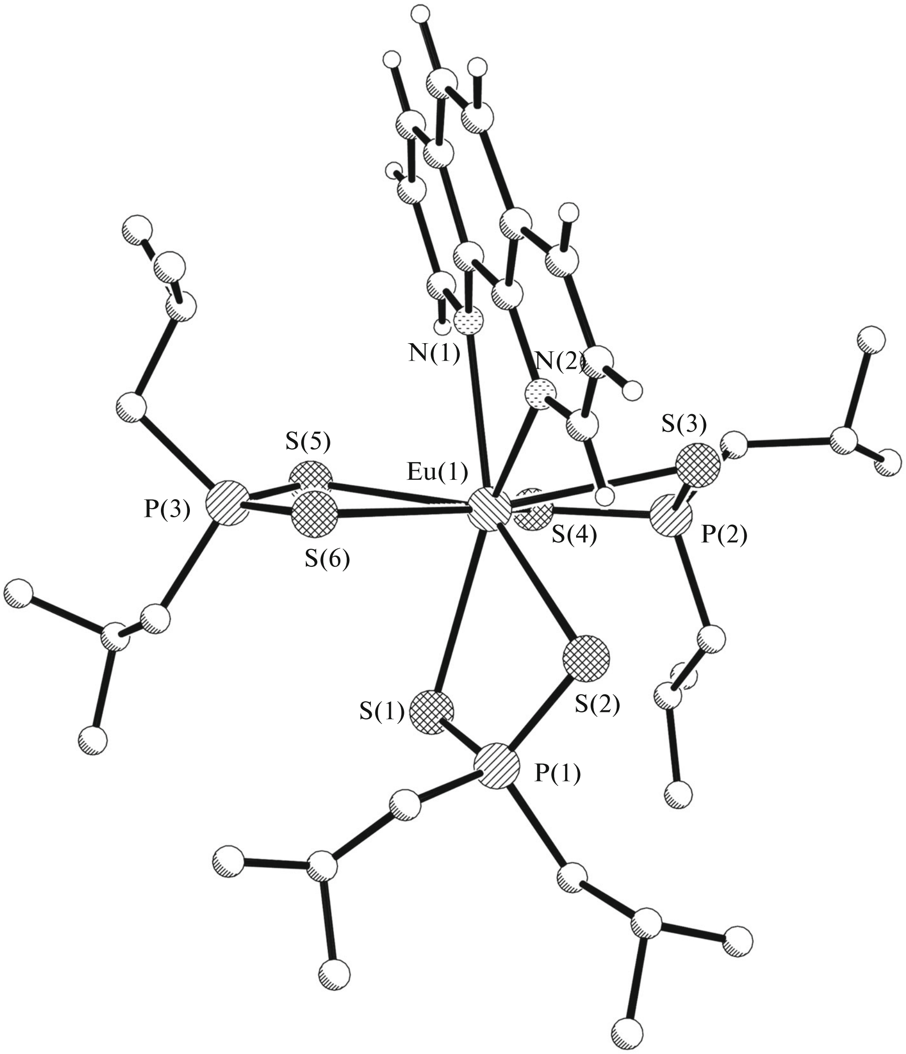

Fig. 6. Molecular structure of complex [Eu(Phen)(i-Bu_2PS_2)$_3$].

structure of this compound consists of molecules of the mononuclear complex. The nitrato group is coordinated by two O atoms. The coordination polyhedron $N_2O_2S_4$ of the Y atom is a distorted trigonal dodecahedron (Fig. 7).

The synthesis of the Nd(III) compound of a similar composition in the presence of orthoethyl formate was described [106]. It was found by the X-ray phase method that the Y(III) and Nd(III) complexes were *i*structural. Single crystals of the compound [Nd(Phen)(i-Bu_2PS_2)$_3$], the synthesis of which was described earlier [104], were obtained by the slow crystallization of the complex [Nd(Phen)(i-Bu_2PS_2)$_2$(NO_3)]. According to the X-ray diffraction data, this complex is *i*structural to [Eu(Phen)(i-Bu_2PS_2)$_3$]. The PL of compounds containing dithiophosphinate ligands was first studied for the complexes [Nd(Phen)(i-Bu_2PS_2)$_2$(NO_3)] and [Nd(Phen)(i-Bu_2PS_2)$_3$] [106]. For the solid samples at 300 K, the PL intensity of the complex [Nd(Phen)(i-Bu_2PS_2)$_3$] is by 1.7 times higher than *I* of [Nd(Phen)(i-Bu_2PS_2)$_2$(NO_3)].

The Eu(III) complexes [Eu(L)(i-Bu_2PS_2)$_2$(NO_3)] (L = Phen, 2,2'-Bipy, 4,4'-Bipy) were obtained [107]. The diffraction pattern of the Phen-containing Eu(III) complex is similar to the diffraction pattern of the Y(III) complex of a similar composition [105]. It is most likely that the coordination polyhedron of the Eu atom is $N_2O_2S_4$. The crystalline samples of the [Eu(L)(i-Bu_2PS_2)$_2$(NO_3)] complexes (L = Phen, 2,2'-Bipy) exhibit the PL at 300 K, and *I* of PL of the complex with Phen is by several times higher than *I* of the complex with 2,2'-Bipy. No photoluminescence of the complexes Eu(4,4'-Bipy)(i-Bu_2PS_2)$_2$(NO_3) and [Eu(L)(i-Bu_2PS_2)$_3$] (L = Phen, 2,2'-Bipy) was detected [107].

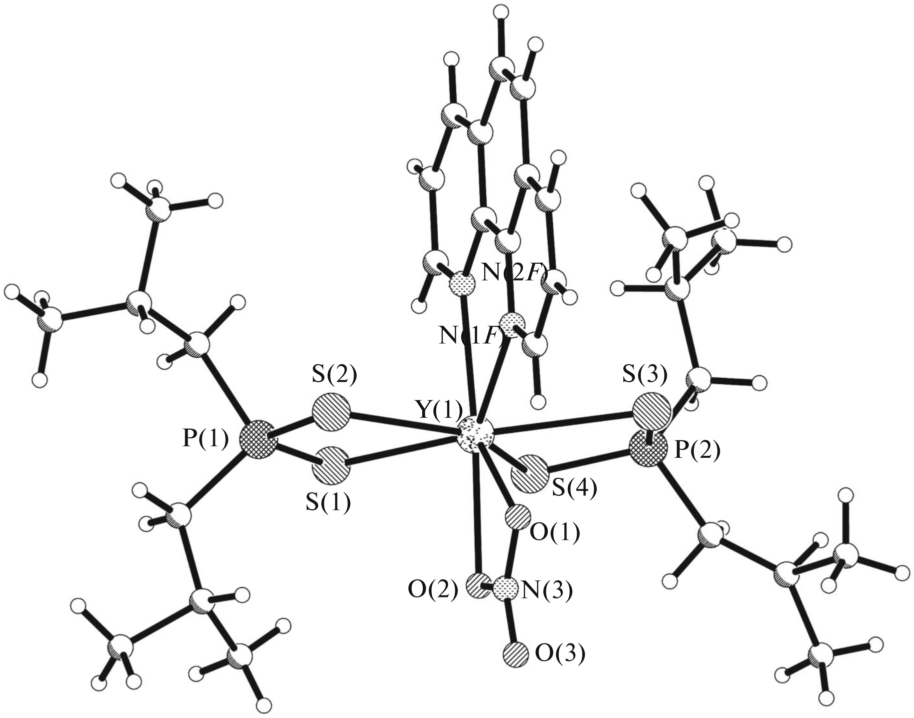

Fig. 7. Molecular structure of complex [Y(Phen)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)].

The crystal structure of the clathrate compound [Sm(Phen)(i-Bu$_2$PS$_2$)$_3$] · MeCN was studied [108], and its single crystals were grown by the slow evaporation of a solution of the complex [Sm(Phen)(i-Bu$_2$PS$_2$)$_3$] obtained using a described procedure [104] in MeCN. According to the X-ray diffraction data, the coordination polyhedron N$_2$S$_6$ of the Sm atom in the mononuclear complex [Sm(Phen)(i-Bu$_2$PS$_2$)$_3$] is the tetragonal antiprism. The crystal structure of the clathrate contains dimeric ensembles of molecules of the mononuclear complex. In addition, the complexes [Sm(L)(i-Bu$_2$PS$_2$)$_3$] (L = Phen, 2,2'-Bipy) in the solid phase at 300 K were found to possess the red-orange PL, and the bands at λ = 600 and 645 nm are most intense in the spectrum. The PL intensity of the Phen-containing complex is by approximately four times higher than *I* of PL of the complex containing 2,2'-Bipy.

The reaction of Ln(NO$_3$)$_3$ · nH$_2$O and i-Bu$_2$PS$_2$Na · 3H$_2$O in i-PrOH or MeCN followed by the filtration of NaNO$_3$ and addition of L (L = Phen, 2,2'-Bipy) at room temperature in air affords heteroligand complexes [Ln(L)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)] (Ln = Sm, Tb, Dy, Tm) [86, 109, 110]. These complexes were obtained in a minor excess of the sulfur-containing ligand (mole ratios Ln^{3+} : i-Bu$_2$PS$_2^-$ are 1 : 3 or 1 : 4). According to the X-ray diffraction data, in single crystals of the complex [Dy(Phen)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)] and *i*structural compounds [Ln(2,2'-Bipy)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)] · C$_6$H$_6$ (Ln = Tb, Tm), the crystal structures are based on molecules of the mononuclear complexes [Ln(L)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)]. The molecular structure of the complex [Tm(2,2'-Bipy)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)] is presented in Fig. 8. As in the complex [Y(Phen)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)] [105], in the above described compounds, the coordination polyhedron LnN$_2$O$_2$S$_4$ is a distorted trigonal dodecahedron. According to the X-ray phase data, the complexes [Ln(Phen)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)] and [Ln(2,2'-Bipy)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)] form two *i*structural series. The synthesized complexes in the solid phase show the PL at 300 K. The PL intensity of the complexes [Ln(Phen)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)] changes in the order: Tb^{3+} > Sm^{3+} ≈ Dy^{3+} (Fig. 9). The complexes of Tm^{3+} ion exhibit very weak PL. A similar situation is observed for the complexes [Ln(2,2'-Bipy)(i-Bu$_2$PS$_2$)$_2$(NO$_3$)]. It was found that in the synthesized complexes Phen exhibits a higher sensitizing ability toward Sm(III) and Tm(III) than 2,2'-Bipy. For the Dy(III) complexes, 2,2'-Bipy is the most efficient sensitizer; for the Tb(III) compounds having the green PL, the sensitizing ability of Phen and 2,2'-Bipy is approximately equal [109, 110].

The reaction of Sm(NO$_3$)$_3$ · 6H$_2$O, i-Bu$_2$PS$_2$Na · 3H$_2$O, and 6,6'-biquinoline (6,6'-Biq) in i-PrOH affords complex [Sm(6,6'-Biq)(i-Bu$_2$PS$_2$)$_3$]$_n$, which is the first example of a coordination polymer for the Ln

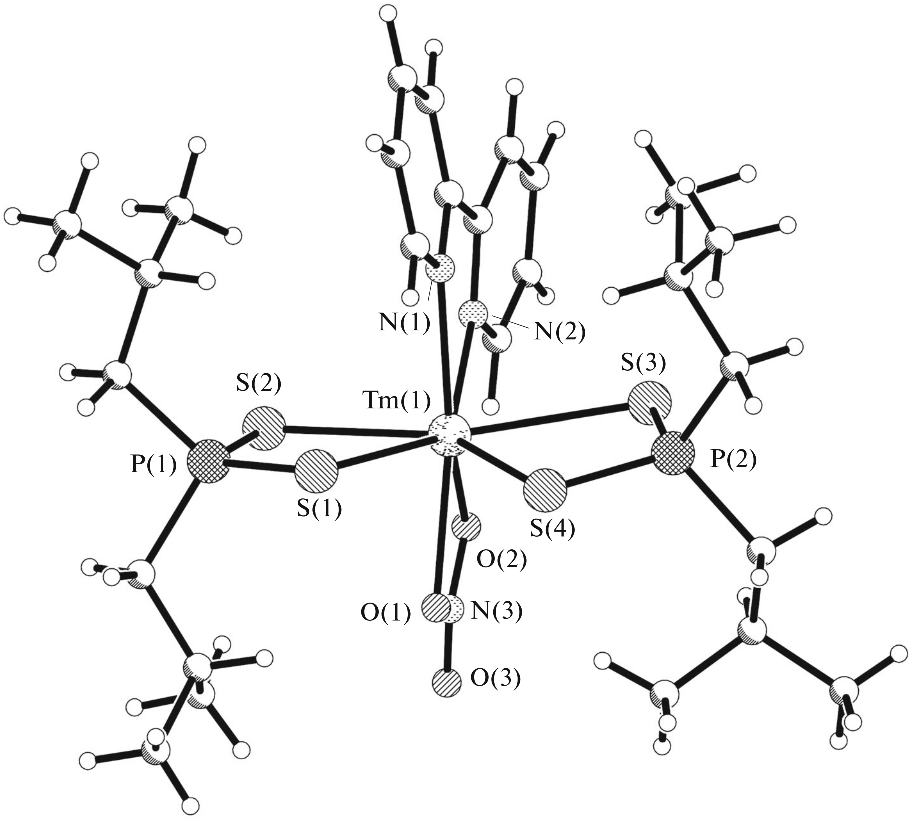

Fig. 8. Molecular structure of complex [Tm(2,2'-Bipy)(i-$Bu_2PS_2)_2(NO_3)$].

complexes with 1,1-dithiolate ligands [111]. According to the X-ray diffraction data, the crystal structure of this compound is built of chains of the Sm(i-$Bu_2PS_2)_3$ fragments and molecules of the bidentate bridging ligand 6,6'-biquinoline (Fig. 10). The coordination sphere of the Sm atom contains six S atoms of three bidentate chelating i-$Bu_2PS_2^-$ ligands and two N atoms of the bidentate bridging ligands 6,6'-Biq. The coordination polyhedron N_2S_6 of the Sm atom is a distorted tetragonal antiprism. The complex was found to exhibit the PL in the solid phase at 300 K.

The number of works devoted to the synthesis and study of the Ln(III) complexes with dithiophosphinate ligands is less than the works on the Ln(III) complexes containing dithiocarbamate ions.

The synthesis and study of the compositions and structures of the Ln dithiophosphinate complexes are of considerable interest for the understanding of chemical reactions that occur in processes of the extraction separation of actinides and lanthanides using dithiophosphinic acids in nitrate media, in particular, to reveal the types of complexes that can be formed upon extraction. A series of works is devoted to the extraction of Ln and extraction separation of lanthanides and actinides using bis(2,2,4-trimethylpentyl)dithiophosphinic acid (Cyanex-301) in nitrate media [112–123]. The most attention was given to the separation of Am(III) and Eu(III). In some works, an additional ligand, namely, tributyl phosphate [114], Phen, or 2,2'-Bipy, was added to the acid [118]. In a number of these articles, solutions of the lanthanide complexes with anions of Cyanex-301 formed in the organic phase upon extraction were studied by physi-

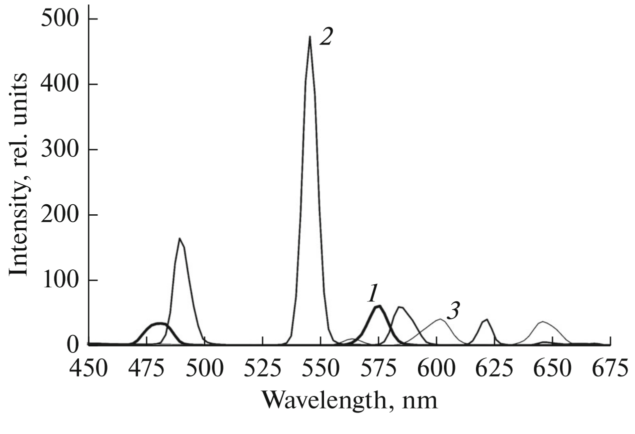

Fig. 9. PL spectra of complexes [Ln(Phen)(i-$Bu_2PS_2)_2(NO_3)$] (Ln = (*1*) Sm, (*2*) Tb, and (*3*) Dy).

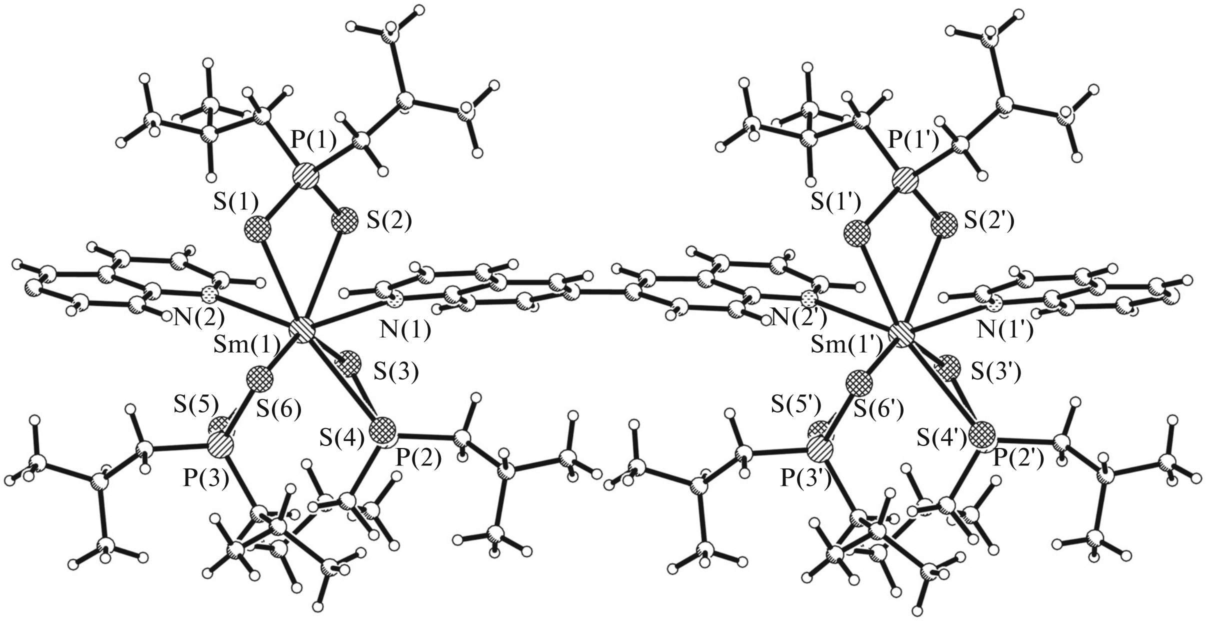

Fig. 10. Fragment of the polymer chain in the crystal structure of compound $[Sm(Biq)(i\text{-}Bu_2PS_2)_3]_n$.

cal methods, and conclusions on the compositions of these complexes were drawn. The tris(chelates) of Nd^{3+}, Sm^{3+}, and Eu^{3+} ions with anions of Cyanex-301 were found in *n*-dodecane [121, 123]. Both the tris(chelates) of Nd^{3+} ion and their dimers were observed in toluene [122]. The La(III), Nd(III), and Eu(III) complexes formed upon extraction to toluene were found to have the formula $HLn(L)_4(H_2O)$ (L = bis(2,4,4-trimethylpentyl)dithiophosphinate ion) [117]. It is assumed [120] that the extraction of La(III), Nd(III), and Eu(III) to toluene results in the formation of the tris(chelates) and also heteroligand complexes containing two dothiophosphinate ligands and NO_3^- ligand. The authors [123] believe that the addition of tributyl phosphate can result in the formation of the heteroligand complex based on the tris(chelate) and tributyl phosphate molecules. Evidently, the available data on the syntheses and structures of the Ln complexes containing anions of dithiophosphinic acids can be useful for the development of the chemistry of extraction processes.

LANTHANIDE COMPLEXES CONTAINING DITHIOPHOSPHATE LIGANDS

Tris(chelates) and complex salts. The synthesis and study of the complex salts $Ph_4As[Ln(S_2P(OEt)_2)_4]$ (Ln = La–Lu, except for Pm) were described [95, 97]. These compounds are formed by the reaction of hydrated Ln(III) chlorides with $NaS_2P(OEt)_2$ and Ph_4AsCl in hot EtOH. The products were recrystallized from a MeCN–*i*-PrOH mixture in air. An attempt to *i*late tris(chelates) $Ln((EtO)_2PS_2)_3$ was unsuccessful [95]. The syntheses of complex salts $Na[Ln(S_2P(OEt)_2)_4]$ (Ln = La–Er) and $NH_4[Ln(S_2P(OEt)_2)_4]$ (Ln = La, Eu) were described [97]. The salts containing Na^+ ion were found to be hygroscopic. In the case of all other salts, the complexes of light Ln(III) are fairly stable in air, and the complexes of heavier Ln(III) are hygroscopic. As compared to similar dithiocarbamate complexes, these dithiophosphates are less sensitive to air moisture. The values of β for a series of the Ln salts (Ln = Pr, Nd, Sm, Dy, Ho, Er, Tm) containing $(EtO)_2PS_2^-$ ligands, ranging from 0.978 to 0.994, differ from the data obtained for the complexes with dithiophosphinate ions [97]. The crystal structures of the salts $Ph_4As[Ln(S_2P(OEt)_2)_4]$ (Ln = La, Er) were determined [124]. In these structures, the Ln atom coordinates eight S atoms at the vertices of the dodecahedron. The synthesis of the salts $Et_4N[Ln((EtO)_2PS_2)_4]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Yb, Ho) in MeOH was described [125].

Tris(chelates) $[La\{S_2P(OR)_2\}_3]$ (R = *n*-Pr, Ph) and $[La\{S_2PO_2G\}_3]$ (G = $-C(CH_3)_2CH_2CH(CH_3)-$, $CH_2C(CH_3)_2CH_2-$, $-C(CH_3)_2C(CH_3)_2-$, $-CH_2CH_2CH(CH_3)-$) were synthesized later by the reaction of anhydrous $LaCl_3$ and the corresponding ammonium dithiophosphate in MeOH [126]. Based on the analysis of the data of IR spectroscopy and ^1H and ^{31}P NMR spectroscopy, the authors [126] assumed that the coordination number of the La atom was 6 in these compounds.

Heteroligand complexes. The dissolution of Ln(III) chloride hydrates and $NaS_2P(OEt)_2$ in EtOH followed by evaporation gives an oil reacting with Ph_3PO in EtOH to form crystalline products $Ln(S_2P(OEt)_2)_3(Ph_3PO)_n$ ($n = 2$ or 3) [95]. The procedure for the synthesis of complexes $Ln(S_2P(OEt)_2)_3(Ph_3PO)_n$ ($n = 2$ for La–Pr and $n = 3$ for Nd–Lu) by the reaction of salt $Na[Ln(S_2P(OEt)_2)_4]$ and Ph_3PO in hot EtOH was proposed [97]. The structures of the heteroligand complex $[La(S_2P(OEt)_2)_3(Ph_3PO)_2]$ and complex salt $[Sm(S_2P(OEt)_2)_2(Ph_3PO)][S_2P(OEt)_2]$ [127] were described. The neutral mononuclear La(III) complex has the coordination polyhedron LaO_2S_6 as a square antiprism. The La atom coordinates six S atoms of three bidentate chelating $(EtO)_2PS_2^-$ ligands and two O atoms of the molecules of the monodentate Ph_3PO ligand. In the complex Sm(III) salt, the central atom coordinates four S atoms of two bidentate chelating $(EtO)_2PS_2^-$ ligands and the O atom of the Ph_3PO molecule at the vertices of the trigonal bipyramid. The structure also contains out-of-sphere $(EtO)_2PS_2^-$ ions. The reactions of the complex salt $Na[Ln((i\text{-}PrO)_2PS_2)_4]$ with L = *N*,*N*-dimethylacetamide (DMA) or *N*,*N*-dimethylformamide (DMF) in di*i*-propyl ether afforded isostructural complexes $[Ln(L)_2((i\text{-}PrO)_2PS_2)_3]$ (Ln = La, Nd) [128]. According to the X-ray diffraction data, the La atom in the $[La(DMA)_2((i\text{-}PrO)_2PS_2)_3]$ complex coordinates six S atoms of three bidentate chelating $i\text{-}PrO)_2PS_2^-$ ligands and two O atoms of the monodentate DMA ligands. The complexes containing $i\text{-}PrO)_2PS_2^-$ ligands and DMSO molecules $[Ln(DMSO)_2((i\text{-}PrO)_2PS_2)_3]$ (Ln = La, Nd) and $[Eu(DMSO)_3((i\text{-}PrO)_2PS_2)_2][Eu((i\text{-}PrO)_2PS_2)_4]$ were synthesized [129]. The X-ray diffraction analysis shows that in the $[La(DMSO)_2((i\text{-}PrO)_2PS_2)_3]$ complex the La atom coordinates six S atoms of three bidentate chelating $(i\text{-}PrO)_2PS_2^-$ ligands and two O atoms of the monodentate DMSO ligands, and the coordination polyhedron LaO_2S_6 is a dodecahedron.

The complexes $[La\{S_2P(OR)_2\}_3 \cdot nL]$ (R = *n*-Pr, Ph) and $[La\{S_2PO_2G\}_3 \cdot nL]$ (G = $-C(CH_3)_2CH_2CH(CH_3)-$, $CH_2C(CH_3)_2CH_2-$, $-C(CH_3)_2C(CH_3)_2-$, $-CH_2CH_2CH(CH_3)-$) ($n = 1$, L = 2,2'-Bipy, Phen; $n = 2$, L = PPh_3) were obtained by the reaction of the corresponding La(III) tris(complexes) and N- or P-donor ligands in benzene [126]. It was found by IR spectroscopy and ^1H and ^{31}P NMR spectroscopy that the La atom in these compounds had the coordination number 8.

The heteroligand dithiophosphate Ln complex with the *N*-heterocycle $Sm(Phen)((i\text{-}PrO)_2PS_2)_3$ was synthesized [86]. The complex was prepared by the reaction of $Sm(NO_3)_3 \cdot 6H_2O$ with $(i\text{-}PrO)_2PS_2K$ and Phen · H_2O in *i*-PrOH (mole ratio 1 : 5 : 1, respectively) at room temperature in air. This complex was found to exhibit the PL in the solid phase at 300 K. The consideration of the PL spectra of the Sm(III) complexes with Phen and different 1,1-dithiolate ligands of the composition $Sm(Phen)(A)_3$ (A = $C_4H_8NCS_2^-$, $i\text{-}Bu_2PS_2^-$ $(i\text{-}PrO)_2PS_2^-$) showed that the PL intensity *I* of these compounds changed in the series of ligands: $i\text{-}Bu_2PS_2^-$ > $i\text{-}PrO)_2PS_2^-$ > $C_4H_8NCS_2^-$. This indicates that the PL intensity *I* can be increased on going from the functional group CS_2 to PS_2 in 1,1-dithiolate ligands (Fig. 11).

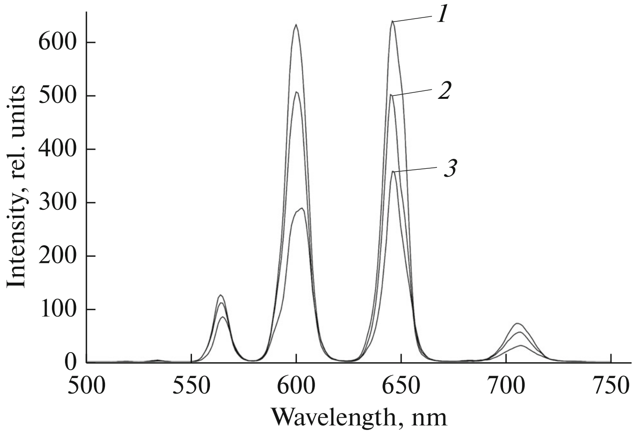

Fig. 11. PL spectra of complexes $Sm(Phen)(A)_3$ (A = (*1*) $i\text{-}Bu_2PS_2^-$, (*2*) $i\text{-}PrO)_2PS_2^-$, and (*3*) $C_4H_8NCS_2^-$).

The synthesis of the Ln complexes with dithiophosphate ions is impeded compared to the dithiocarbamate and dithiophosphinate Ln(III) complexes. This is related, most likely, to a decrease in the electron-donor ability of the dithiophosphate ligands [130].

Thus, significant success was achieved for the synthesis of various types of coordination Ln compounds with the 1,1-dithiolate ligands. In the most cases, organic solvents were used in the syntheses. Several substances were synthesized in an inert atmosphere. At the same time, the obtained results [67, 68, 75, 82] indicate that the heteroligand complexes can also be prepared in an aqueous medium. According to the X-ray diffraction data, the coordination number 6 is observed in the Ln tris(chelates) with the bulky $(C_6H_{11})_2PS_2^-$ ligand. In the case of the complex salts and heteroligand Ln compounds with 1,1-dithiolate ligands, the Ln^{3+} ions are characterized by a coordination number of 8. In some works, the data of electronic spectroscopy indicate a comparatively low contribution of covalence to the Ln–ligand bonds [30, 39, 83, 97]. The role of covalence in the Ln–dithiophosphinate ligand bond was considered in [119, 120, 131]. Some complexes were established to be promising precursors for the preparation of films and nanosized particles of lanthanide sulfides. The preparation of the films and nanoparticles of EuS and SmS is especially interesting. In particularly, this is indicated in the review [132]. Several complexes demonstrate valuable functional properties (luminescence, magnetic, and catalytic). Finally, the data on the character of the complex formation of lanthanides and actinides with 1,1-dithiolate ligands are interesting for the understanding of the extraction processes aimed at separating these groups of elements. The data presented indicate that further investigations on the syntheses of coordination compounds of lanthanides with 1,1-dithiolate ligands and studies of their structures and functional properties are promising.

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